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Japanese Kokai Patent Application No. Hei 5[1993]-170909

in-situ
Condensation
of
Silane is
described & claimed.

Method for making of
dispersion of granular
fluoropolymers.

J

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METHOD FOR MANUFACTURING AQUEOUS DISPERSION OF GRANULAR POLYMERS

Abstract

Objective

To provide a method for manufacturing an aqueous dispersion of granular polymers prepared by making composites of polysiloxane and a fluoropolymer with improved weather resistance, stain resistance, and adhesion to inorganic substrates.

Constitution

An aqueous dispersion of granular polymers can be prepared by a condensation reaction of 1.0-300 parts by weight of organosilane in the presence of 100 parts by weight (solid content) of an aqueous dispersion of a granular fluoropolymer, for example, a granular vinylidene fluoride polymer and/or granules containing a vinylidene fluoride polymer.

Claims

1. Method for manufacturing aqueous dispersion of granular polymers, characterized by a condensation reaction of 1.0-300 parts by weight of organosilane in the presence of 100 parts by weight (solid content) of an aqueous dispersion of a granular fluoropolymer.

2. Method for manufacturing an aqueous dispersion of granular polymers according to Claim 1, characterized in that the aqueous dispersion of the granular fluoropolymer is obtained

3
the
condensation
not claimed

by an emulsion polymerization of 10-900 parts by weight of monomers comprising

(a) an acrylic acid alkyl ester with a C₁₋₅ alkyl group and/or methacrylic acid alkyl ester with a C₁₋₅ alkyl group 10-99.9#wt%,

(b) ethylenic unsaturated carboxylic acid 0.1-60#wt%, and

(c) another monomer which can polymerize with monomers (a) and (b) 0-89.9#wt% in an aqueous medium

Detailed description of the invention

[0001]

Industrial application field

The present invention pertains to a method for manufacturing an aqueous dispersion of granular polymers, and particularly pertains to a method for manufacturing an aqueous dispersion of granular polymers which can form coating films that have excellent weather resistance, stain resistance, and adhesion to inorganic substrates.

[0002]

Prior art

In recent years, from the viewpoint of preventing harm to the environmental such as through air pollution caused by organic solvents and its adverse effect on the human body, and the saving of natural resources, the shift from traditional use

of organic solvent solutions of fluoropolymers to aqueous dispersions of fluoropolymers which use water as the dispersion medium has been discussed actively.

[0003]

However, from the viewpoint of physical properties, aqueous dispersions of fluoropolymers are inferior to fluoropolymer solutions using organic solvents, and in particular they are inferior in weather resistance, stain resistance, and adhesion to inorganic substrates.

[0004]

The following reasons may be the main causes of the above-mentioned drawbacks of aqueous dispersions of fluoropolymer.

[0005]

In aqueous dispersions of fluoropolymers, the polymers are dispersed and they are in the form of granules, therefore to stabilize them, various water-soluble components such as a dispersion stabilizer, soap, alkali, etc., are necessary. Therefore, at the time of forming coating films, these water-soluble components remain on the surface of the coating films and reduce the resistance of the coating films to weathering and staining and the adhesion of the coating films to inorganic substrates.

[0006]

Conversely, in fluoropolymer solutions which are prepared by using organic solvents, the polymers are in solution and it is possible to form molecular-level coating films which are not in granular form and moreover, a dispersion stabilizer, soap, water-soluble component such as alkali, etc. are unnecessary, therefore coating film formability, weather resistance, stain resistance, and adhesion to inorganic substrates are more excellent than those of aqueous dispersions of fluoropolymers.

[0007]

To ease such drawbacks of aqueous dispersions of fluoropolymers, the optimization of the monomer compositions of the aqueous dispersions of fluoropolymers, reduction of the granule size, preparation of composites of granules with a core/shell structure, and improvement by addition of water-soluble solvents to a water medium have been tried. However in actuality, they have been not yet been sufficiently improved.

[0008]

Problems to be solved by the invention

The present invention was carried out to solve the conventional problems and its objective is to provide a method for manufacturing aqueous dispersions of granular polymers which are prepared by making composites of polysiloxanes with

fluoropolymers which improve weather resistance, stain resistance, and adhesion to inorganic substrates.

[0009]

Means to solve the problems

The present invention pertains to a method for manufacturing an aqueous dispersion of granular polymers, characterized by the condensation reaction of 1.0-300 parts by weight of an organosilane in the presence of 100 parts by weight (solid content) of an aqueous dispersion of a granular fluoropolymer.

[0010]

In the present invention, through the condensation reaction of an organosilane in the presence of an aqueous dispersion of a granular fluoropolymer, an aqueous dispersion of the fluoropolymer and polysiloxane granules can be obtained. By using the thus obtained aqueous dispersion, coating films with excellent weather resistance, stain resistance, and adhesion to inorganic substrates can be formed.

[0011]

In the following, the present invention will be described in detail.

[0012]

Fluoropolymers

For the fluoropolymers used in the present invention, vinylidene fluoride polymers can be preferably used. Examples of the vinylidene fluoride polymers include vinylidene fluoride homopolymer, monomers which can copolymerize with vinylidene fluoride such as fluorine-containing ethylenic unsaturated compounds such as trifluorochloroethylene, hexafluoropropylene, tetrafluoroethylene, vinyl fluoride, hexafluoroisobutylene, perfluoroacrylic acid, etc.; ethylenic unsaturated compounds containing no fluorine such as cyclohexyl vinyl ether, hydroxyethyl vinyl ether, etc.; dienes containing no fluorine such as butadiene, isoprene, chloroprene, etc. The proportion of vinylidene fluoride to be used in vinylidene fluoride polymers is usually at least 30 wt% of the polymers. Among the vinylidene fluoride polymers, vinylidene fluoride homopolymer, vinylidene fluoride/tetrafluoroethylene copolymer, vinylidene fluoride/tetrafluoroethylene/hexafluoropropylene copolymer are preferable, and especially vinylidene fluoride/tetrafluoroethylene/hexafluoropropylene copolymer is preferably used. The proportions of the monomers in the copolymer are 30-90 wt% of vinylidene fluoride, 50-9 wt% of tetrafluoroethylene, and 20-1 wt% of hexafluoropropylene. The molecular weight of the vinylidene fluoride polymer is usually 10,000 to 500,000.

[0013]

As long as a fluoropolymer can be dispersed in an aqueous medium as granules, it can be added in any condition; however, in the present invention the fluoropolymer which can be obtained by emulsion polymerization is preferable, and in this case since it can be prepared as an aqueous dispersion it is convenient to use it as is for an aqueous dispersion in a condensation reaction. Such an aqueous dispersion of the fluoropolymer can be prepared using a common emulsion polymerization, for example, emulsion polymerization of starting monomers in the presence of an emulsifier, a polymerization initiator, a pH-adjusting agent, etc., which are usually used in an aqueous medium.

[0014]

The granule size of the fluoropolymer depends on the granule size of the objective polymer; however, it is usually preferably 0.05-3 μm .

[0015]

In the present invention, granular fluoropolymers can be used as is; however, by using the fluoropolymer as seeds and absorbing or adsorbing mainly (meth)acrylic acid ester and carrying out so-called seed polymerization to obtain fluorine/acrylic polymer granules (hereinafter referred to as fluorine/acrylic polymer granules), then the thus obtained fluorine/acrylic polymer granules can be preferably used. In

seed polymerization, it is preferable that the (meth)acrylic acid ester is made of the following (a)-(c) components.

(a) (meth)acrylic acid alkyl ester with a C_{1-5} alkyl group

The amount of component (a) to be used is 10-99.9 wt%, preferably 30-60 wt%, based on the total monomers,

(b) ethylenic unsaturated carboxylic acid

The amount of component (b) to be used is 0.1-60 wt%, preferably 10-40 wt% based on the total monomers, and

(c) another monomer which can polymerize with monomers (a) and (b)

The amount of component (c) to be used is 0-89.9 wt%, preferably 0-40 wt%, more preferably 0-30 wt% based on the total monomers.

[0016]

By using such fluorine/acrylic polymer granules, the weather resistance and pollution resistance of the coating films and adhesion to inorganic base materials to the coating films can be improved more than when fluoropolymer alone is used.

[0017]

In the above-mentioned component (a), examples of the acrylic acid alkyl ester with a C₁₋₅ alkyl group include methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, amyl acrylate, and isoamyl acrylate. Among these acrylates, acrylic acid alkyl esters with C₁₋₃ alkyl groups, especially acrylic acid alkyl esters with C₁₋₂ alkyl groups are preferable.

[0018]

Examples of the methacrylic acid alkyl ester with a C₁₋₅ alkyl group include methyl methacrylate, ethyl methacrylate, propyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, amyl methacrylate, isoamyl methacrylate, etc. Among them, methacrylic acid alkyl esters with C₁₋₃ alkyl groups, especially methacrylic acid alkyl esters with C₁ or C₂ alkyl groups are preferable.

[0019]

Examples of the ethylenic unsaturated carboxylic acid of the above-mentioned component (b) include acrylic acid, methacrylic acid, itaconic acid, fumaric acid crotonic acid, etc., and especially acrylic acid is preferably used.

[0020]

Examples of the above-mentioned component (c) include vinyl compounds such as vinyl acetate; amide compounds such as acrylamide, methacrylamide, N-methyl acrylamide, N-methyl methacrylamide, N-methylol acrylamide, N-methylol methacrylamide, N-alkyl acrylamide, N-alkyl methacrylamide, N,N-dialkyl acrylamide, N,N-dialkyl methacrylamide, etc.; acrylic acid ester such as 2-hydroxyethyl acrylate, N-dialkylaminoethyl acrylate, glycidyl acrylate, fluoroalkyl acrylate, etc.; methacrylic acid ester such as dialkylaminoethyl methacrylate, fluoroalkyl methacrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, ethylene glycol dimethacrylate, etc.; vinyl ether such as allyl glycidyl ether; conjugated diene such as 1,3-butadiene, isoprene, etc.; aromatic vinyl compounds such as styrene, α -methylstyrene, halogenated styrene, etc.; divinyl compounds such as divinylbenzene, etc.; vinyl cyanide such as acrylonitrile, methacrylonitrile, etc. Among them, N-methylol acrylamide, N-methylol methacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, allyl glycidyl ether, 1,3-butadiene, styrene, acrylonitrile, etc. are preferably used.

[0021]

(A) In the presence of 100 parts by weight (solid matter) of an aqueous dispersion of the above-mentioned granular fluoropolymer, 10-900 parts by weight, preferably 40-400 parts by weight, more preferably 100-300 parts by weight of monomers comprising the above-mentioned components (a), (b), and (c) are

*Notes
25-50%
Fluoropolymer
in A.M.F.*

polymerized, whereby the monomers are absorbed or adsorbed by the granular fluoropolymer, preferably absorbed by the fluoropolymer and polymerized to give an aqueous dispersion (B) of granules containing fluoropolymer.

[0022]

The aqueous dispersion of the granular polymer of the present invention can be prepared by the condensation of an organosilane compound in the presence of the aqueous dispersion (B) of granules containing fluoropolymer.

[0023]

Organosilane compounds

For the above-mentioned organosilane compounds, alkoxysilane compounds which can be represented by the general formula $R_nSi(OR')_{4-n}$ or cyclic siloxanes which can be represented by $R_mSiO(4-m)_2$ can be given.

[0024]

In the above-mentioned formulas, R and R' are C_{1-8} organic groups such as alkyl groups, for example, methyl group, ethyl group, n-propyl group, and isopropyl group, and others such as γ -chloropropyl group, vinyl group, 3,3,3-trifluoropropyl group, γ -glycidoxypropyl group, γ -methacryloxypropyl group,

γ -mercaptopropyl group, phenyl group, 3,4-epoxycyclohexylethyl group, γ -aminopropyl group, etc. In the formulas n is an integer 0-3, and m is an integer 0-3.

[0025]

Examples of the alkoxysilane compounds include tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane, methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, n -propyltrimethoxysilane, n -propyltriethoxysilane, isopropyltrimethoxysilane, isopropyltriethoxysilane, γ -chloropropyltrimethoxysilane, γ -chloropropyltriethoxysilane, vinyltrimethoxysilane, γ -methylacryloxypropyltriethoxysilane, γ -mercaptopropyltrimethoxysilane, γ -mercaptopropyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, γ -aminopropyltrimethoxysilane, 3,4-epoxycyclohexylethyltrimethoxysilane, 3,4-epoxycyclohexylethyltriethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, diethyldimethoxysilane, etc. Preferably tetramethoxysilane, tetrathoxysilane, methyltrimethoxysilane, methyltriethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane are used.

[0026]

Examples of cyclic siloxanes include hexaphenylcyclotrisiloxane, octaphenylcyclotetrasiloxane, tetravinyltetramethylcyclotetrasiloxane,

hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, pentamethylcyclotetrasiloxane, hexamethylcyclotetrasiloxane, tetramethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, trimethyltriphenylcyclotrisiloxane, etc. In addition to the cyclic siloxanes, there are straight-chain or branched-chain organosiloxanes.

[0027]

These organosiloxanes may be used alone or as a mixture of at least two and a metal alkoxide such as titanium alkoxide and aluminum alkoxide can be jointly used with the organosiloxanes. If necessary, these organosiloxanes may be dissolved in organic solvents before they are used.

[0028]

The amount of organosiloxane compound to be used with respect to the aqueous dispersion of granular fluoropolymer (hereinafter referred to as polymer seed) is 1-300 parts by weight, preferably 5-150 parts by weight, more preferably 10-100 parts by weight based on 100 parts by weight (solid matter) of the polymer seed.

[0029]

Condensation reaction

The aqueous dispersion media used in the manufacturing method of the present invention include water alone, or ketones, lower alcohols, esters, etc. which are miscible with water. The amount of these organic solvents to be used can be 1-100 wt% with respect to water, however, for maintaining good dispersion of the polymer seed it is preferably less than 70 wt%, more preferably less than 50 wt%.

[0030]

In the present invention, the absorption of organosilane compounds by polymer seeds can be carried out easily by adding the organosilane compounds to aqueous dispersions of the polymer seeds, followed by thorough stirring.

[0031]

To make the polymer seeds efficiently absorb the organosilane compound, if necessary it is possible in advance to make the polymer seeds absorb a solvent whose solubility in water is 10^{-3} wt% or less. It is desirable to add and absorb the organocompounds under the conditions in which the pH of the system is adjusted to 4-10, preferably 5-9, more preferably 6-8, and the temperature is 90°C or less, preferably 70°C or less, more preferably 50°C or less, most preferably 30°C or less.

[0032]

The condensation reaction of organosilane compounds can be controlled easily by adjusting the reaction temperature and hydrogen ion concentration, thereby the degree of polymerization of the organosilane compounds can be controlled.

[0033]

The condensation reaction of organosilane compounds can be carried out usually at 30°C or greater, preferably 50°C or greater, more preferably 80°C or greater, and for example it can be carried out in the presence of an emulsifier. The emulsifier not only plays the role of a surfactant but also functions simultaneously as a catalyst for the condensation reaction of the organosilane compound. For such an emulsifier, an aliphatic substituted benzenesulfonic acid is preferably used.

[0034]

In the present invention, the condensation reaction may be carried out either under the condition that the organosilane compound is absorbed by the polymer seeds or under the condition that the organosilane compound is not absorbed by the polymer seeds, for example, under the condition that organosilane compound is adsorbed by the polymer seeds. However, to obtain composite granules with excellent compatibility, it is preferable that a portion or all of the organosilane compound is absorbed by the polymer seeds the condensation reaction is carried out. At that time the amount of the organosilane

compound absorbed by the polymer seeds to carry out the condensation reaction is preferably at least 5 wt%, more preferably at least 10 wt%, most preferably at least 30 wt% based on the total organosilane compound used.

[0035]

Application examples

Next, application examples will be used to better explain the present invention. The "parts" and the "%" in the examples are all "parts by weight" and "wt%", respectively.

[0036]

Application Example 1

The air inside a 7-L-capacity separatory flask was replaced by nitrogen, then 100 parts of vinylidene fluoride polymer (vinylidene fluoride/tetrafluoroethylene/hexafluoropropylene copolymer, average granule size: 0.25 μm , trade name: KYNAR 9031, Atochem Co.) shown in the Application Example 1 of Table I and 0.3 part of sodium persulfate were put in the flask and then the temperature was raised to 75°C.

[0037]

An emulsion was prepared in another vessel using 50 parts of methyl methacrylate 25 parts of ethyl acrylate, 15 parts of butyl acrylate, 5 parts of styrene, 5 parts of acrylic acid (all

shown in Application Example 1 of Table I), 50 parts of water, and 1.0 part of sodium alkylbenzenesulfonate (emulsifier), and then the emulsion was added to the above-mentioned separatory flask continuously over a 3 h period. After the completion of the addition, the mixture was aged at 85°C-95°C for 2 h, cooled to finish the reaction to give a vinylidene fluoride copolymer.

[0038]

Next, under the condition of maintaining the temperature at 25°C, the pH of the system was adjusted to 8.0 and 30 parts of the alkoxysilane shown in Application Example 1 of Table I was added and then it was vigorously stirred for about 30 min. Then the temperature of the reaction vessel was raised to 70°C and reacted for 3 h to give an aqueous dispersion of a granular polymer. No formation of aggregates was observed in the dispersion and after standing for a long time there was no separation of the dispersed granules, therefore it was confirmed that a stable dispersion was maintained.

[0039]

Application Examples 2-10 and Comparative Examples 1-4

Polymerization was carried out using the chemicals shown in Table I, Table II, and Table III and the same method as that used in Application Example 1 was used to prepare the aqueous dispersions of a granular polymer of Application Examples 2-10

→ Condensation of vinylidene fluoride polymerization (Coul.)
for methacrylate
(functional)

and Comparative Examples 1-4. Like the dispersion of Application Example 1, no aggregates were formed in the thus-obtained dispersions and the stability of the dispersions was excellent.

[0040]

Table I

	① 実 施 例				
	1	2	3	4	5
② フッ化ビニリデン系重合体	100	100	100	100	100
③ (単量体組成)					
④ メタクリル酸メチル	50	50	50	50	10
⑤ アクリル酸エチル	25	25	25	25	10
⑥ アクリル酸ブチル	15	15	15	15	-
⑦ スチレン	5	5	5	5	75
⑧ アクリル酸	5	5	5	5	5
⑨ 単量体合計量 (部)	100	100	100	100	100
⑩ (アルコキシシラン化合物)					
⑪ メチルトリエトキシシラン	30	250	-	-	30
⑫ ジメチルジエトキシシラン	-	-	100	-	-
⑬ 1-ナトリウムジプロピルジエトキシシラン	-	-	-	100	-
⑭ (塗料としての評価結果)					
⑮ 耐候性	○	○	○	○	○
⑯ 密着性	○	○	○	○	○
⑰ 耐汚染性	○	○	○	○	○
⑱ 耐水性	○	◎	◎	◎	○
⑲ 撥水性 (接触角°)	85	92	89	90	79
⑳ 耐久性	○	○	○	○	○
㉑ 鉛筆硬度	H	2H	2H	2H	2H
㉒ 成膜性	○	◎	◎	○	○

Key:	1	Application Example
	2	Vinylidene fluoride polymer
	3	Composition of monomer
	4	Methyl methacrylate
	5	Ethyl acrylate
	6	Butyl acrylate
	7	Styrene
	8	Acrylic acid
	9	Sum of monomers (parts)
	10	Alkoxysilane compound
	11	Methyltriethoxysilane
	12	Dimethyldiethoxysilane
	13	(γ -methacryloxypropyl)trimethoxysilane
	14	(Results of evaluation as a coating material)
	15	Weather resistance
	16	Adhesion
	17	Staining resistance
	18	Water resistance
	19	Water repellency (contact angle in degrees)
	20	Durability (permanence)
	21	Pencil hardness
	22	Film formability

Table II

	① 実 施 例				
	6	7	8	9	10
② フッ化ビニリデン系重合体	100	100	100	100	100
③ (単量体組成)					
④ メタクリル酸メチル	74	250	-	-	-
⑤ アクリル酸エチル	-	125	-	-	-
⑥ アクリル酸ブチル	4	75	-	-	-
⑦ スチレン	17	25	-	-	-
⑧ アクリル酸	5	25	-	-	-
⑨ 単量体合計量 (部)	100	500	-	-	-
⑩ (アルコキシシラン化合物)					
⑪ メチルトリエトキシシラン	30	30	30	-	-
⑫ ジメチルジエトキシシラン	-	-	-	100	-
⑬ 1-ナタリウムプロピルトリメチルシラン	-	-	-	-	30
⑭ (塗料としての評価結果)					
⑮ 耐候性	○	○	○	○	○
⑯ 密着性	○	○	△	△	△
⑰ 耐汚染性	○	○	○	○	○
⑱ 耐水性	○	○	○	○	○
⑲ 撥水性 (接触角°)	88	78	92	95	92
⑳ 耐久性	○	○	○	○	○
㉑ 鉛筆硬度	H	H	F	H	F
㉒ 成膜性	○	△	○	△	○

Key:	1	Application Example
	2	Vinylidene fluoride polymer
	3	(Composition of monomer)
	4	Methyl methacrylate
	5	Ethyl acrylate
	6	Butyl acrylate
	7	Styrene
	8	Acrylic acid
	9	Sum of monomers (parts)
	10	(Alkoxysilane compound)
	11	Methyltriethoxysilane
	12	Dimethyldiethoxysilane
	13	(γ -Methacryloxypropyl)trimethoxysilane
	14	(Results of evaluation as a coating material)
	15	Weather resistance
	16	Adhesion
	17	Contamination resistance
	18	Water resistance
	19	Water repellency (contact angle in degrees)
	20	Durability (permanence)
	21	Pencil hardness
	22	Film formability

Table III

	① 比較例			
	1	2	3	4
② フッ化ビニリデン系重合体	100	100	100	100
③ (単量体組成)				
④ メタクリル酸メチル	50	50	50	—
⑤ アクリル酸エチル	25	25	25	—
⑥ アクリル酸ブチル	15	15	15	—
⑦ スチレン	5	5	5	—
⑧ アクリル酸	5	5	5	—
⑨ 単量体合計量 (部)	100	100	100	0
⑩ (アルコキシシラン化合物)				
⑪ メチルトリエトキシシラン	—	400	30	—
⑫ ジメチルジエトキシシラン	—	—	—	—
⑬ 1-メタクリルオキシプロピルトリメトキシシラン	—	—	—	—
⑭ (塗料としての評価結果)				
⑮ 耐候性	△	○	×	×
⑯ 密着性	○	×	△	×
⑰ 耐汚染性	△	○	×	×
⑱ 耐水性	△	△	△	△
⑲ 撥水性 (接触角°)	60	78	42	69
⑳ 耐久性	○	○	△	△
㉑ 鉛筆硬度	H B	H	H	4 B
㉒ 成膜性	△	×	○	×

Key: 1	Comparative Example
2	Vinylidene fluoride polymer
3	(Composition of monomer)
4	Methyl methacrylate
5	Ethyl acrylate
6	Butyl acrylate
7	Styrene
8	Acrylic acid
9	Sum of monomers (parts)
10	(Alkoxysilane compound)
11	Methyltriethoxysilane
12	Diethylmethoxydiethoxysilane
13	(γ -methacryloxypropyl)trimethoxysilane
14	(Results of evaluation as a coating material)
15	Weather resistance
16	Adhesion
17	Contamination resistance
18	Water resistance
19	Water repellency (contact angle in degrees)
20	Durability (permanence)
21	Pencil hardness
22	Film formability
22	#1 Acrylic polymer

(Evaluation of aqueous dispersion of granular polymer)

Titanium oxide (trade name: Tipaque R930, Ishihara Sangyo Kaisha, Ltd.) as a filler	50 parts
Polycarbonate sodium salt (trade name: SN-DISPERSANT 5044, San Nopco Ltd.) as a dispersing agent	2 parts
Ethylene glycol as an antifreeze	1 part
Preservative (trade name: SN-215, San Nopco Ltd.)	0.05 part

Antifoaming agent (trade name: FOAMASTER-AP,

San Nopco Ltd.)

0.5 part

2-amino-2-methyl-1-propanol

2 parts

were added to 100 parts (solid matter) of an aqueous dispersion of granular polymers obtained in the above-mentioned application examples and comparative examples, and after the solid content was adjusted to 60 wt%, the viscosity of the coating material was adjusted to 4000 cps with hydroxyethylcellulose (trade name: A-5000, Fuji Chemical Co.) as a thickener. Mixing was carried out using a dispersion mixer and after thorough mixed it was transferred to a vacuum deaerator for deaeration.

[0041]

The thus-obtained coating material was coated in such a way on an iron plate (JIS-G3141, SPCC plate, 0.8 x 70 x 150 mm) which had been degreased with xylene and an alkaline detergent that a 200- μ m-thick coating film was obtained after drying with an airless spray gun. The coated iron plate was dried at 150°C for 15 min.

[0042]

The following tests were carried out for the thus-obtained coated iron plate. the results are shown in Tables I, II, and III.

① Weather resistance

The percentage of the retention of gloss after putting a sample to be tested in a fade meter (Suga Shikenki Co., Ltd.) for 1000 h with respect to the initial gloss was calculated and then the weather resistance of the sample was graded according to the following 3 levels.

[0043]

O: 100-80
Δ: 79-40
X: less than 39.

② Adhesion

The coated surface was cross-cut (2-mm square 10 x 10), then a peeling test was carried out using adhesive tape. The adhesion was graded according to the following 3 levels.

[0044]

Number of squares remaining on the cut surface

O: 100-80
Δ: 79-40
X: less than 39.

③ Staining resistance

A paste-like mixture made by mixing (weight ratio: 1:2) carbon powder with glycerin was coated uniformly on the surface of a coating film, and then it was allowed to stand for 24 h.

Then the coating film was washed with water, and the washing off of the stains was visually observed and then it was graded according to the following 3 levels.

[0045]

O: the stains were completely washed off.

[0046]

Δ: some stains remained

[0047]

X: considerable amount of stains remained.

④ Water resistance

It was evaluated according to the condition of the coating film after immersion in distilled water (20°C) for 24 h.

[0048]

(Thickness of the coating film: 500 μm)

⊙: Excellent

O: Good

Δ: fair

X: poor

⑤ Water repellency (contact angle)

A device for measuring the contact angle (Elma Kogaku Co., Ltd.) was used to measure the contact angle of a coating film.

⑥ Durability (permanence)

A nut (M-6) was dropped on a coating film through a 2-m high vinyl pipe at 60 degree angle, and the weight of the nut which exposed the iron plate was measured, and the durability was evaluated according to the following 3 levels:

[0049]

O: at least 30 kg

Δ: 11 kg-30 kg

X: 10 kg or less

⑦ Pencil hardness

It was measured using the method described in JIS-K5400, 6-14.

⑧ Film formability

A coating material was coated on an aluminum substrate using an applicator in such a way that a 30- μ m-thick coating film was obtained, then it was dried at ordinary temperature for 2 weeks to give a coating film. The evaluation of the

formability of the coating film was carried out visually and it was graded according to the following 3 levels.

[0050]

O: no cracks of the coating film

Δ: some cracking observed

X: cracking observed all over the coating film

Application Examples 1-10 are examples of aqueous coating materials using the aqueous dispersions within the scope of the claims of the present invention, and good characteristics, which are the objective of the present invention, are obtained.

[0051]

Comparative Example 1 is an example in which an alkoxysilane compound was not used, and its weather resistance and stain resistance are inferior.

[0052]

Comparative Example 2 is an example wherein the amount of alkoxysilane compound used is greater than that prescribed in the claims of the present invention, and especially the adhesion and film formability are inferior, and moreover the performance corresponding to the amount added was not obtained.

[0053]

Comparative Example 3 is an example wherein an aqueous dispersion of a granular polymer was used which polymer being obtained by the procedure of Application Example 1 except that 100 parts of acrylic ester copolymer latex (AB316(A), Japan Synthetic Rubber Co., Ltd.) were used instead of using granular vinylidene fluoride polymer. In this comparative example, weather resistance and many characteristics are inferior.

[0054]

Comparative Example 4 is an example wherein an alkoxysilane was not used, and all characteristics are inferior.

[0055]

Effect of the invention

According to the present invention, after organosilanes are added to fluoropolymers followed by carrying out a condensation reaction of the organosilanes, it is possible to manufacture aqueous dispersions with the characteristics of fluoropolymers and the characteristics of polysiloxanes, thus novel aqueous dispersions can be manufactured easily.

[0056]

The aqueous dispersions of granular polymers obtained by the present invention can form coating films which are excellent

in weather resistance, adhesion, stain resistance, water repellency, water resistance, etc. therefore in addition to various coating materials, they can be suitably used in electrocoating, fiber-treating materials, paper-converting materials, floor-coating materials, etc.

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AN 1994:194202 CAPLUS

DN 120:194202

TI Manufacture of aqueous emulsions of fluoropolymers

IN Yoshino, Hiroyuki; Nishiwaki, Koichi; Shimizu, Tatsuya; Kasai,

Kyoshi

PA Japan Synthetic Rubber Co Ltd, Japan

SO Jpn. Kokai Tokkyo Koho, 10 pp.

CODEN: JKXXAF

PI JP 05271359 A2 931019 Heisei

AI JP 92-97306 920325

DT Patent

CC 42-10 (Coatings, Inks, and Related Products)

Section cross-reference(s): 35

AB In manuf. of the title emulsions by emulsion polymn. of 20-400 parts radically polymerizable monomers contg. $\geq 50\%$ C1-18 alkyl (meth)acrylates in the presence of 100 parts fluoropolymer particles with av. particle size 0.05-3 μm contg. $\geq 30\%$ vinylidene fluoride (I). $\geq 50\%$ of the radically polymerizable monomers are added in aq. dispersions of the fluoropolymer particles before initiation of the polymn. Thus, 70% of a monomer mixt. contg. Me methacrylate 50, Et acrylate 25, Bu acrylate 15, styrene 5, and acrylic acid 5 parts and Na alkylbenzenesulfonate was added in an aq. dispersion contg. 100 parts 1-tetrafluoroethylene-hexafluoropropylene copolymer (I content 60%, particle size 0.25 μm ; Kynar 9031), aged at 80.degree. for 1 h, K2S2O8 added, heated for 2 h, blended with residual monomer mixt., and further heated at 85-95.degree. for 2 h to give a graft fluoropolymer acrylic dispersion. 100 parts (as solid) of which was blended with coating additives, dild. with H2O, sprayed on a SPCC plate (JIS G 3134), and dried at 150.degree. for 15 min to form a coating showing pencil hardness 2 H and good transparency and resistances to weathering, water, staining, alkali, and acid.

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AN 1994:10473 CAPLUS

DN 120:10473

TI Aqueous dispersions of granular fluoropolymer-polsiloxane copolymers

IN Shimizu, Tatsuya; Nishiwaki, Koichi; Yoshino, Hiroyuki; Kasai, Kyoshi

PA Japan Synthetic Rubber Co Ltd, Japan

SO Jpn. Kokai Tokkyo Koho, 10 pp.

CODEN: JKXXAF

PI JP 05170909 A2 930709 Heisei

AI JP 91-355973 911220

DT Patent

LA Japanese

AB The title dispersions are prepd. by condensing 1-300 parts organosilanes in the presence of 100 parts (solids) aq. granular fluoro olymg. 10-900 parts monomers contg. C1-5 alkyl (meth)acrylates 10-99.9, ethylenically unsatd. carboxylic acids 0.1-60, and comonomers 0-89.9% in the presence of 100 parts (solids) aq. dispersions of granular vinylidene fluoride polymers. Thus, 100 parts